

# PREPARATION OF PT-RU OR PT-MO SUPPORTED CATALYSTS FOR PEM OR DIRECT METHANOL FUEL CELLS FROM SINGLE-SOURCE MOLECULAR PRECURSORS

C. M. Lukehart<sup>1</sup>, D. L. Boxall<sup>1</sup>, J. D. Corn<sup>1</sup>, M. Hariharasarma<sup>1</sup>, W. D. King<sup>1</sup>, K. C. Kwiatkowski<sup>1</sup>, E. S. Steigerwalt<sup>1</sup>, and E. A. Kenik<sup>2</sup>

(1) Department of Chemistry, Vanderbilt University, Nashville, TN 37235

(2) Metals and Ceramic Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

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## ABSTRACT

An overview of the synthesis and characterization of several Pt-Ru or Pt-Mo/Vulcan carbon nanocomposites and one Pt-Ru/graphitic carbon nanofiber nanocomposite is provided. Each binary metal alloy nanocluster composition is accessed through the thermal decomposition of a single-source molecular precursor containing the desired metal stoichiometry. Microwave heating techniques are used to form a Pt-Ru/Vulcan carbon nanocomposite within one minute of thermal treatment. The metal stoichiometry of individual alloy nanoparticles has been determined from on-particle EDS measurements obtained using HR-TEM(FEG) instrumentation. Preliminary DMFC testing results are also summarized.

## INTRODUCTION

There is currently much interest in developing metal alloy catalysts having improved reactivity as anode catalysts in fuel cells.<sup>1</sup> Specifically, Pt-Ru alloys are commonly used as anode catalysts in direct methanol fuel cells (DMFCs) for the electrocatalytic oxidation of methanol.<sup>2</sup> Pt-Mo catalysts are of interest as anode catalysts in PEM fuel cells operating on reformate fuels due to their higher CO-tolerance relative to platinum metal catalysts.<sup>3</sup> Even though fuel cell anode catalysts might undergo significant chemical changes during conditioning or aging within a working fuel cell environment, there is a need to determine the dependence of fuel cell catalytic activity on the precise metal alloy stoichiometry of the initial catalyst as prepared. For practical considerations, there is interest in preparing fuel cell anode catalysts on conducting carbon supports to minimize the amount of noble metal required in a working fuel cell.

We are investigating the use of single-source molecular precursors as a means to better control the elemental stoichiometry of individual metal alloy nanoparticles formed on conducting carbon supports. While others have used heteronuclear clusters to prepare ruthenium-rich Pt-Ru/carbon nanocomposites of low total metal weight percent,<sup>4</sup> we have used heteronuclear noncluster or cluster compounds to prepare several Pt-Ru or Pt-Mo/carbon nanocomposites having high total metal loading and a platinum atomic percent of 50% or greater. In this report, we provide (1) an overview of the synthesis and characterization of several Pt-Ru or Pt-Mo/Vulcan carbon nanocomposites, (2) the rapid synthesis of a Pt,Ru/Vulcan carbon nanocomposite using microwave heating, (3) the synthesis of a Pt,Ru/graphitic carbon nanofiber (GNF) nanocomposite, (4) the determination of the metal alloy stoichiometry of individual alloy nanoclusters, and, (5) preliminary results from testing selected Pt-Ru/Vulcan carbon nanocomposites as DMFC anode catalysts.

## EXPERIMENTAL

The single-source molecular precursors  $[(\eta^3\text{-}\eta^3\text{-2,7-dimethyloctadienediyl})\text{RuCl}(\mu\text{-Cl})_2\text{PtCl}]$ , **1** ( $L = \text{PPh}_3$ ,  $\text{PEt}_3$ , or ethylene),<sup>5</sup>  $[\text{Cl}_2\text{Pt}(\mu\text{-bipyrimidine})\text{Ru}(2,2'\text{-bipyridine})_2][X]_2$ , **2** ( $X = \text{BF}_4$  or  $\text{PF}_6$ ),<sup>6</sup>  $[\text{Pt}_3(\text{PPh}_2\text{CH}_2\text{PPh}_2)_3\{\text{HgRu}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2][\text{PF}_6]_2$ , **3**,<sup>7</sup>  $[\text{Ru}\{\mu\text{-2,3-bis(2-pyridyl)-quinoxaline}(\text{PtCl}_2)_3\}[\text{BF}_4]_2$ , **4**,<sup>8</sup>  $[\text{Pt}(\text{pyridine})_2[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ , **5**,<sup>9</sup>  $[\text{Pt}(1,5\text{-cyclo-octadiene})(\text{Me})[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ , **6**,<sup>10</sup>  $[\text{Pt}(\text{PPh}_2\text{CH}_2\text{PPh}_2)_3\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})][\text{BPh}_4]$ , **7**,<sup>11</sup> where prepared by literature procedures, modifications of literature procedures, or by novel methods. Carbon supports included Vulcan<sup>TM</sup> Carbon XC-72R (Cabot Corporation) or GNFS prepared using published procedures.<sup>12</sup>

Metal alloy/carbon nanocomposites were prepared by depositing single-source molecular precursors from a solution onto the appropriate carbon support through evaporation of the solvent. Multiple depositions were sometimes employed. Thermal degradation of the deposited molecular precursors typically occurred in reactive [air (up to 350°C) and/or getter gas (350-650°C)] or inert [nitrogen (650-700°C)] gaseous environments. Thermal treatments were conducted either in a tube furnace using gas flow rates typically of 150 mL/min and heating rates typically of 15°C/min or in a microwave oven (Sharp Corporation, Model R-2M52B) operating at 2.45 GHz with a fixed power level of 600 Watts. Samples prepared by microwave heating were contained in a vial surrounded by a thermal bath of Vulcan carbon. Chemical microanalysis was performed by Galbraith Laboratories, Knoxville, TN.

Low-resolution TEM micrographs were obtained using a Philips CM20T transmission electron microscope operating at 200 kV and equipped with an EDAX detector, while HR-TEM micrographs and on-particle EDS spectra were obtained at ORNL using a Philips CM200FEG

TEM operating at 200 kV and equipped with an Oxford light element EDS detector and an EMISPECT Vision data acquisition system. Powder XRD scans were obtained on a Scintag X1 diffraction system.

## RESULTS

As shown in Table I, complexes **1** ( $L=C_2H_4$ ), **2** ( $X=BF_4$ ), **3**, and **4** which have Pt/Ru metal stoichiometries of 1:1, 1:1, 3:2, and 3:1, respectively, serve as single-source molecular precursors for Pt-Ru/Vulcan carbon nanocomposites having metal alloy fcc lattice constants consistent with those observed for bulk Pt-Ru alloys containing the same respective Pt/Ru metal ratios. These nanocomposites have metal loadings of 25-39 weight percent and metal alloy nanoparticle average diameters of 2.7-7.5 nm (as volume-weighted average diameters determined from XRD peak widths) or 2.6-5.7 nm (as number-averaged diameters determined from TEM micrographs). Only monomodal histograms of metal alloy particle sizes are observed.

**Table I. Analysis of Selected Pt-Ru/Vulcan Carbon Nanocomposites**

<i>Metal Alloy Composition</i>	<i>Molecular Precursor</i>	<i>Total M wt. %</i>	<i>Ave. Dia. (nm) (XRD/TEM)</i>	<i>fcc <math>a_{obs}</math> (Å)</i>	<i>fcc <math>a_{expected}</math> (Å)</i>
Pt <sub>1</sub> Ru <sub>1</sub>	<b>1</b> ( $L=C_2H_4$ )	39	2.7/2.6	3.858(6)	3.864
Pt <sub>1</sub> Ru <sub>1</sub>	<b>2</b> ( $X=BF_4$ )	33	4.2/4.3	3.86(1)	3.864
Pt <sub>3</sub> Ru <sub>2</sub>	<b>3</b>	25	7.5/3.9	3.875(2)	3.876
Pt <sub>3</sub> Ru <sub>1</sub>	<b>4</b>	37	6.7/5.7	3.911(1)	3.895

As shown in Table II, complexes **5**, **6**, and **7** which have Pt/Mo metal stoichiometries of 1:2, 1:1, and 3:1, respectively, serve as single-source molecular precursors for Pt-Mo/Vulcan carbon nanocomposites having bulk metal analyses consistent with the Pt-Mo content of the respective molecular precursor. The value of the fcc lattice constants observed for these alloy nanocomposites is not a reliable indicator of Pt/Mo composition due to the very similar atomic radii of Pt and Mo. Full-profile Rietveld refinement of the powder XRD scans of these pure nanocomposites reveals best convergence at Pt/Mo ratios near to the metal content of the molecular precursors. These nanocomposites have metal loadings of 43-58 weight percent and metal alloy nanoparticle average diameters of 3.9-12.2 nm (as determined from XRD peak widths) or ca. 3.5 nm (as determined from TEM micrographs). Only monomodal histograms of metal alloy particle sizes are observed.

**Table II. Analysis of Selected Pt-Mo/Vulcan Carbon Nanocomposites**

<i>Metal Alloy Composition</i>	<i>Molecular Precursor</i>	<i>Total M wt. %</i>	<i>Ave. Dia. (nm) (XRD/TEM)</i>	<i>fcc <math>a_{obs}</math> (Å)</i>	<i>Pt:Mo Ratio by ICP-OES</i>
Pt <sub>1</sub> Mo <sub>2</sub>	<b>5</b>	58	12.2/3.5	3.9144(1)	0.5
Pt <sub>1</sub> Mo <sub>1</sub>	<b>6</b>	52	3.9/...	3.9183(1)	0.9
Pt <sub>3</sub> Mo <sub>1</sub>	<b>7</b>	43	4.6/3.4	3.9124(1)	2.9

Deposition of molecular precursor **1** ( $L=C_2H_4$ ) having a Pt:Ru stoichiometry of 1:1 onto Vulcan carbon followed by microwave irradiation under appropriate gaseous atmospheres over a total heating period of less than 60 seconds gives the expected Pt<sub>1</sub>Ru<sub>1</sub>/carbon nanocomposite. A TEM micrograph of one such nanocomposite is shown in Figure 1. HR TEM micrographs reveal lattice fringes on the Pt<sub>1</sub>Ru<sub>1</sub> particles consistent with a 1:1 alloy composition. A histogram of Pt<sub>1</sub>Ru<sub>1</sub> nanoparticle diameters reveals an average nanocluster diameter of 3.2 nm with a standard deviation of 0.66 nm and a size distribution of only ca. 1.4 nm at full-width-at-half-height. The Pt<sub>1</sub>Ru<sub>1</sub> nanoclusters give a diffraction pattern consistent with a fcc cell exhibiting broad peaks as expected from the small average particle size of the Pt<sub>1</sub>Ru<sub>1</sub> nanoclusters. Peak positions give a fcc lattice parameter of 3.867 Å, as expected for a 1:1 Pt:Ru alloy (see Table I).

Pt<sub>1</sub>Ru<sub>1</sub> nanoclusters can also be formed on GNF carbon supports using complex **1** ( $L=C_2H_4$ ) as a single-source molecular precursor. Deposition of this precursor onto a GNF support followed by the appropriate thermal treatment gives a Pt<sub>1</sub>Ru<sub>1</sub>/GNF nanocomposite, as shown in Figure 2. The metal alloy nanocrystals are highly dispersed on the GNF support.

The on-particle Pt:Ru metal stoichiometry of several Pt-Ru/Vulcan carbon nanocomposites prepared from single-source molecular precursors has been determined by EDS measurements using HR-TEM(FEG) microscopy. Pt:Ru atomic ratios obtained as raw data were corrected for an apparent loss of Ru from the outermost layer of the individual particles. A plot of these corrected Pt:Ru atomic ratios for a number of individual alloy particles of one such sample is shown in Figure 3. The major contribution to the experimental uncertainties shown is the error associated with the counting statistics of the detector.

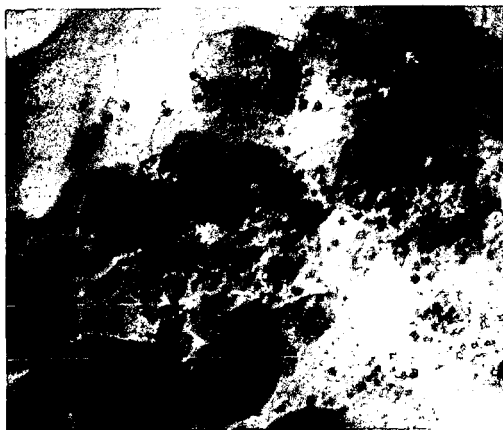


Figure 1. TEM micrograph of a Pt,Ru/Vulcan carbon nanocomposite prepared by microwave heating.



Figure 2. TEM image of a Pt,Ru/GNF nanocomposite prepared using **1** ( $L-C_2H_4$ ) as a single-source precursor for the alloy nanoclusters.

Such on-particle EDS measurements typically indicate that the Pt:Ru atomic ratio of individual metal alloy particles fall within one or two standard deviations of the bulk Pt:Ru elemental stoichiometry. As shown in Table III, the calculated weighted average of Pt:Ru atomic ratios determined from individual alloy nanoclusters within four different alloy/Vulcan carbon nanocomposites fall close in value to the bulk alloy stoichiometry as determined by chemical microanalysis. The experimental uncertainty of alloy compositions determined by chemical microanalysis has not been determined.

Selected Pt-Ru/Vulcan carbon nanocomposites prepared using complexes of type **1** or **2** as single-source molecular precursors have been tested as anode catalysts in DMFCs. Details of these testing procedures will be presented elsewhere. One such Pt,Ru/Vulcan carbon nanocomposite exhibited a higher activity for methanol oxidation at open circuit and at low current densities than did a comparable commercial catalyst, while another Pt,Ru/Vulcan carbon nanocomposite outperformed a comparable commercial catalyst at all higher current densities.

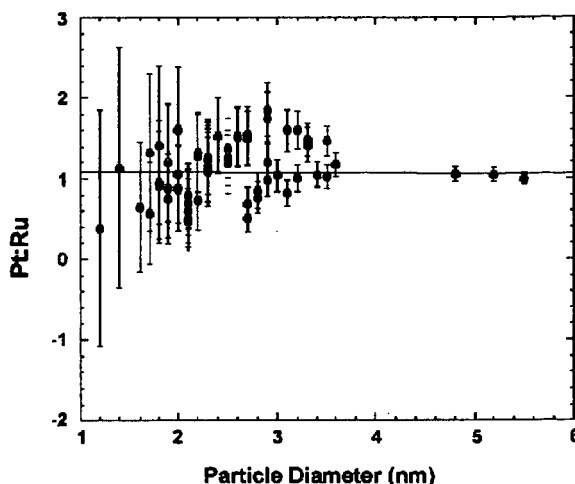


Figure 3. Corrected Pt:Ru atomic ratios for individual metal alloy nanoparticles as a function of nanoparticle size.

**Table III.** Comparison of Pt:Ru Atomic Ratios Determined by Chemical Analysis and by On-Particle EDS Analysis

<i>Alloy/Vulcan C. Nanocomposite</i>	<i>D<sub>TEM</sub> (nm)</i>	<i>D<sub>EDS</sub> (nm)</i>	<i>Chemical Analysis (Pt/Ru<sub>1</sub>)</i>	<i>Average EDS (Pt/Ru<sub>1</sub>)</i>
<b>Pt<sub>1</sub>Ru<sub>1</sub></b>	3.4 (0.9)	2.6 (0.8)	1.08	1.11 (0.03)
<b>Pt<sub>1</sub>Ru<sub>1</sub></b>	-----	2.4 (0.4)	----	1.00 (0.06)
<b>Pt<sub>1</sub>Ru<sub>1</sub></b>	2.6 (0.9)	3.0 (0.8)	0.90	0.88 (0.04)
<b>Pt<sub>1</sub>Ru<sub>1</sub></b>	5.7 (3.1)	3.2 (0.7)	3.20	2.83 (0.11)

## DISCUSSION

Seven heteronuclear noncluster or cluster complexes have been successfully used as single-source molecular precursors for the preparation of Pt-Ru or Pt-Mo/Vulcan carbon nanocomposites in which the metal stoichiometry of the molecular precursor provides significant control over the metal content of the resulting binary metal alloy nanoclusters. Thermogravimetric analysis of the thermal decomposition of the heptanuclear precursor **3** reveals a single mass-loss event corresponding to loss of the mercury content of the precursor. This result indicates that volatile main group metals can serve as bridging atoms in cluster precursors without being incorporated stoichiometrically into the resulting alloy nanocluster. In addition, this synthetic strategy can be used to prepare metal alloy/Vulcan carbon nanocomposites having high metal loading while maintaining relatively small average particle sizes for the alloy phase. Independent determination of the metal stoichiometry of metal alloy nanoclusters using full-profile Rietveld analysis of XRD patterns is possible and is typically reliable to within a 5 weight % variation of the content for each metal.

Pt<sub>1</sub>Ru<sub>1</sub>/Vulcan carbon nanocomposites can be prepared very rapidly (<1 min) from deposited single-source molecular precursors using microwave heating of the conductive, particulate support. Normal thermal processing of deposited precursors to give binary metal alloy/Vulcan carbon nanocomposites using tube furnace heating requires typically 2-4 hours of thermal treatment. In addition to the rapid formation of the nanocomposite, microwave heating apparently minimizes metal diffusion on the carbon support to afford metal alloy nanoclusters having more narrow particle size distributions. The general scope of this synthetic method is being investigated.

The successful formation of Pt<sub>1</sub>Ru<sub>1</sub>/GNF nanocomposites using a single-source molecular precursor is a unique method for obtaining metal alloy nanoclusters on a support having defined structural variety. GNFs can be prepared in which the graphite planes are oriented parallel, perpendicular, or in a herringbone pattern relative to the long axis of the carbon nanofiber. Growth of metal alloy nanoclusters on such ordered carbon supports provides an opportunity to study metal nanocluster-carbon matrix effects and DMFC activity as a function of the atomic and electronic structure of the carbon support. Such studies are under active investigation.

A critical factor in evaluating the practicality of preparing metal alloy nanoclusters by any synthetic method is the direct determination of the metal stoichiometry of individual alloy nanoparticles. By using HR-TEM(FEG) techniques, the metal stoichiometry of individual Pt-Ru alloy nanoclusters has been determined. Preliminary data indicate that metal alloy nanocluster composition is controlled to a high degree by the metal stoichiometry of the single-source precursor used in the synthesis. Further study of truly on-particle metal analysis will explore the general validity of this synthetic method. The observation of a partial loss of Ru during these on-particle analyses was unexpected. Interestingly, the extent of this Ru loss is dependent on alloy particle size and can usually be corrected for by assuming Ru loss from only the outermost unit cell thickness of the metal nanocluster. Due to the known volatility of ruthenium oxides, these results are consistent with the known presence of oxidized Ru species on the surfaces of Pt-Ru nanoparticles.<sup>13</sup> More detailed confirmation of this observation is anticipated. On-particle analysis of the metal alloy stoichiometry of the Pt-Mo/Vulcan carbon nanocomposites mentioned above (as well as others) is also under investigation.

## CONCLUSIONS

Metal alloy/carbon nanocomposites can be formed using single-source molecular precursors to provide considerable control of the metal stoichiometry of the resulting binary metal nanocluster phase. Rapid thermal treatment using microwave heating affords metal alloy/carbon nanocomposites in which the metal nanoclusters have relatively narrow particle size distributions. True on-particle metal stoichiometries can be measured using HR-TEM(FEG) techniques; however, a correction for metal loss possibly due to the presence of surface oxidized species might be necessary for very small alloy particles. Study of the general scope of using this synthetic strategy to prepare binary, ternary, or higher order metal alloys is underway.

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